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Unconventional Hydrocarbon Fuels

J. Timothy Bays (PI), David L. King, Kristin H. Jarman, John C. Linehan, Molly J. O'Hagan, Christina Sorensen

Pacific Northwest National Laboratory

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U.S. DEPARTMENT OF ENERGY

Overview

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Timeline

- Fundamental research project supporting DOE/ industry fuels-technologies projects
- Project milestones and deliverables are evaluated annually

Budget

Project funded by DOE/VT:

FY14: $150K

FY15: $150K

Barriers (from DOE/VT MYPP 2011-2015)

- Apply chemical structure analysis to assess the impact of fuels on the deterioration rates and durability of engine fuel systems.
- Develop models which correlate fuel structure with fuel properties or fuel effects, such as lubricity and seal swell.

Partners

- Coordinating Research Council
- CanmetENERGY
- Red Leaf Resources, Inc.

Relevance and Project Objectives

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- Overall Objectives:
  1. Facilitate the successful introduction of fuel feedstocks compatible with future advanced combustion engines to help reduce the U.S. dependence on foreign oil.
  2. Develop analytical approaches correlating fuel component molecular structure to fuel properties and fuel performance.
- Objective (October 2014 through March 2015): Utilize one- and two-dimensional nuclear magnetic resonance (NMR) spectroscopy, and gas chromatographic techniques, to correlate fuel sub-structures with fuel properties.

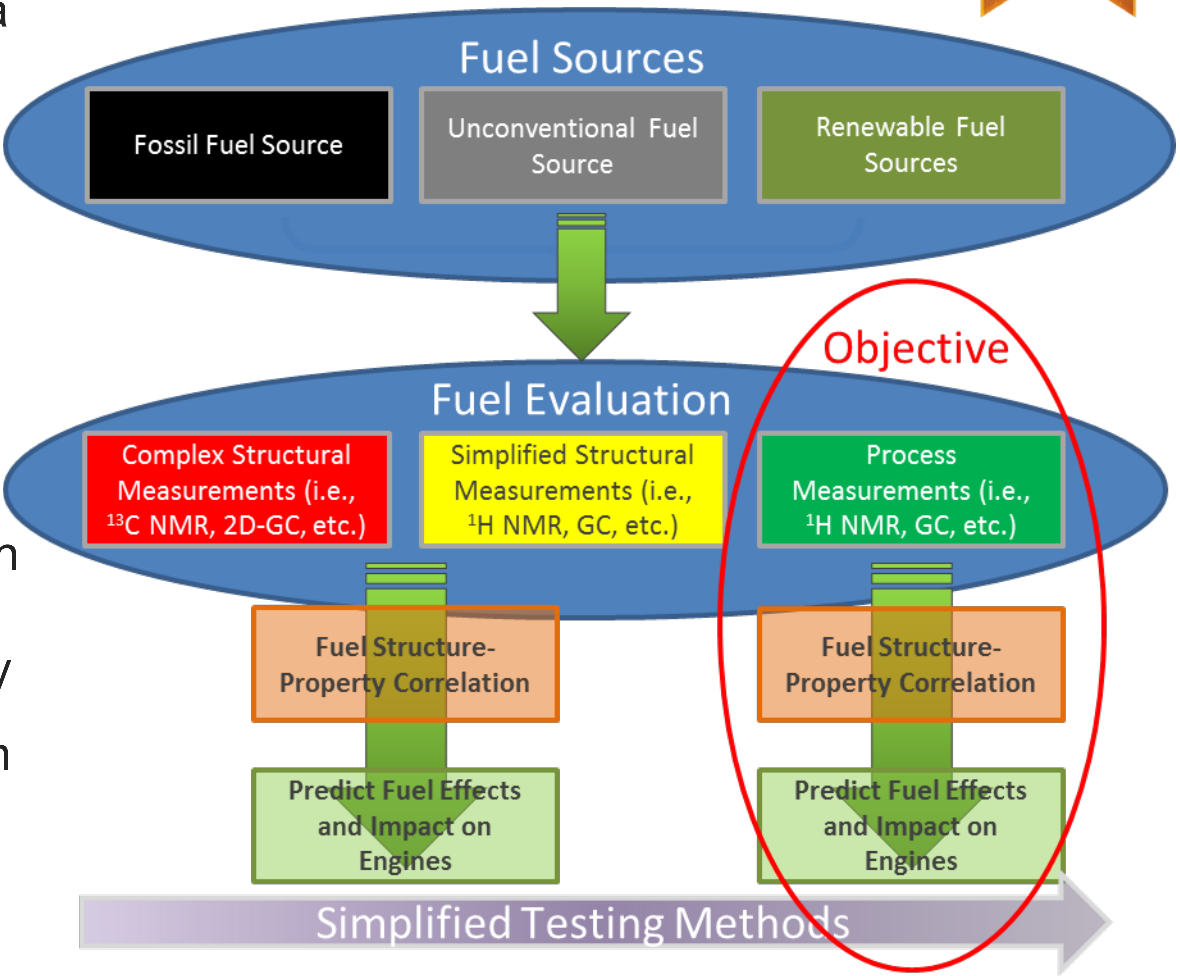
- *Project addresses barriers by examining unconventional fuel sources and assessing chemical sub-structure differences from conventional fuels, and the impact of those sub-structures on fuel properties and engine fuel systems.*

Milestones

Date	Milestone	Status
June 2014	Complete two-dimensional NMR data collection for structure-property correlations within available fuel set.	Complete
December 2014	Identify study fuel set and begin collection of NMR spectra and GC chromatography.	Complete
March 2015	Complete data collection efforts on study fuel set.	Complete
September 2015	1. Model fuel properties, mapping features to properties. 2. Submit a publication outlining characteristic fuel features, that can be attributed to molecular structural contributions, associated with a group of diesel fuels, that can be correlated with a fuel performance property or bulk property described by an ASTM standard test.	On Track

Approach/Strategy

- Analyze fuel samples from a wide variety of sources
- Assess characteristic fuel structures and sub-structures
- Correlate sub-structure populations with fuel properties
- Correlate sub-structures with fuel effects and impact on engine fuel system durability
- Reduce measurements from complex to simple while maintaining prediction fidelity



Technical Accomplishments
--Fuel Processing Characterization

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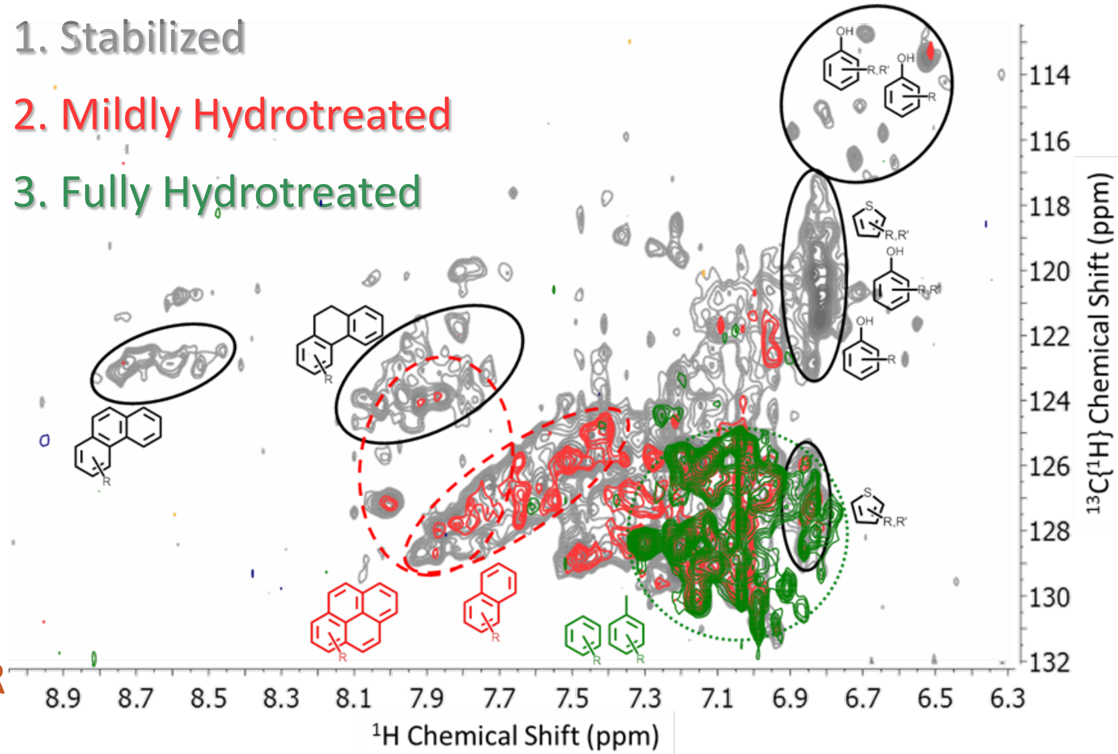
- Examine shale oil at different process stages
- 2D NMR reduces spectral overlap and reveals otherwise hidden features
- Valuable insights into fuels and feedstocks
- Clear changes in fuel composition can be observed at each stage of upgrading
- Preliminary comparison with commercial Diesel #2 shows structural commonality, but also differences.

Conclusion: Combinations of 2D NMR and other techniques provide insights into fuel processing. These can be extended to feedstock properties and process analysis.

Overlay of Three, 2D NMR Spectra*
of #2 Diesel, Derived from Shale Oil,
Showing Fuel Composition Changes During Upgrading



*Single-Bond Proton-Carbon Correlation (HSQC) NMR Spectra

Shale Oil samples obtained from Red Leaf Resources, Inc. and upgraded by Intertek PARC.

Technical Accomplishments
-- Fuel Characterization

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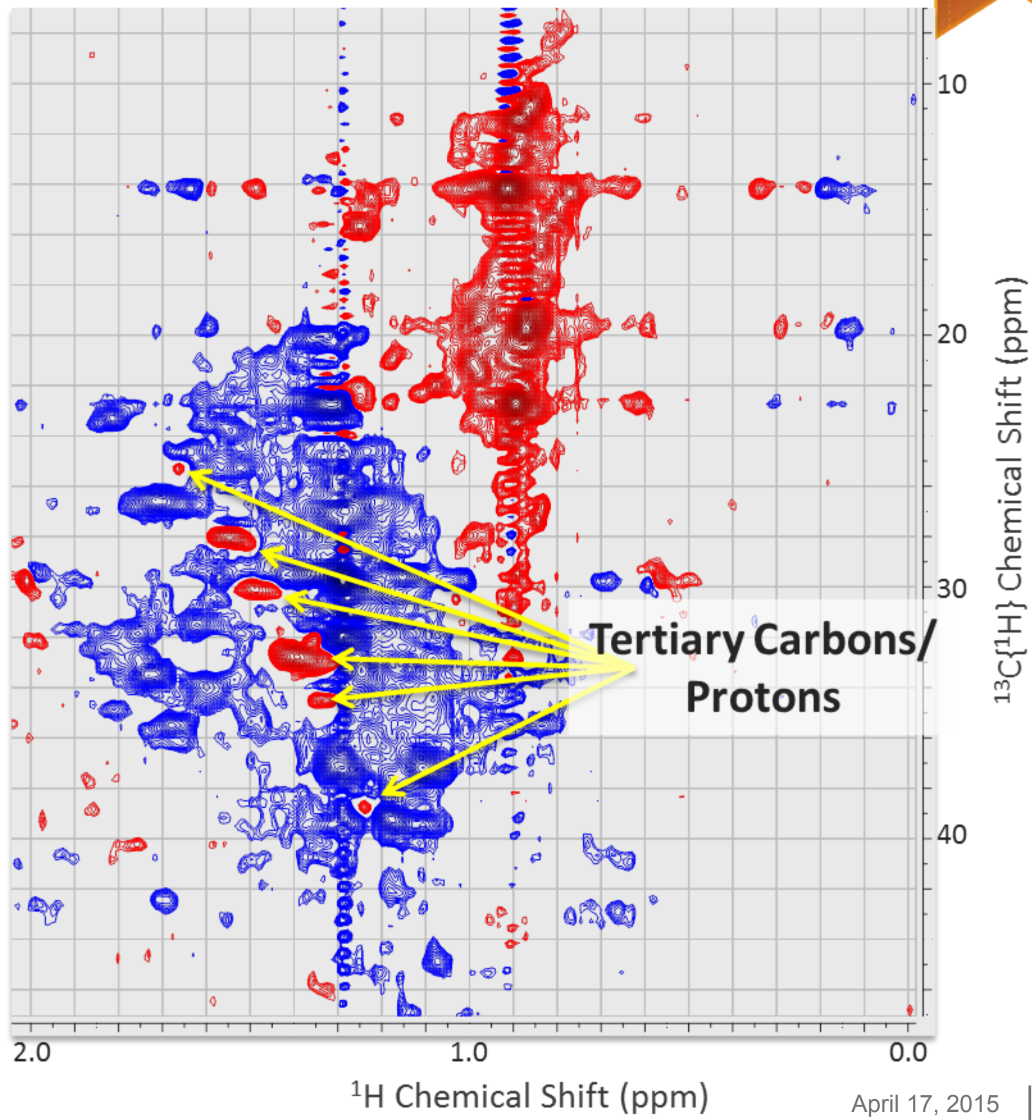
- Tertiary Carbon Census
  - Tertiary carbons = highly substituted carbons with 3 carbons and 1 hydrogen attached
  - Supports inclusion of a 2-methyl paraffin as a surrogate fuel component
  - Site most susceptible to auto-oxidation, impacting:
    - Fuel Stability
    - Gum Formation
    - IQT Measurements
    - Octane
  - Impacts addition of fuel stabilizers

Conclusion: Better fuel characterization allows robust input for modeling routines, generating correlations with actionable outputs to predict fuel properties and fuel effects.



ULSD sample obtained and analyzed as part of the CRC Advanced Alternative Renewable Fuels and the Surrogate Diesel Fuels Projects

Technical Accomplishments
-- Predictive Tools for Fuel Properties

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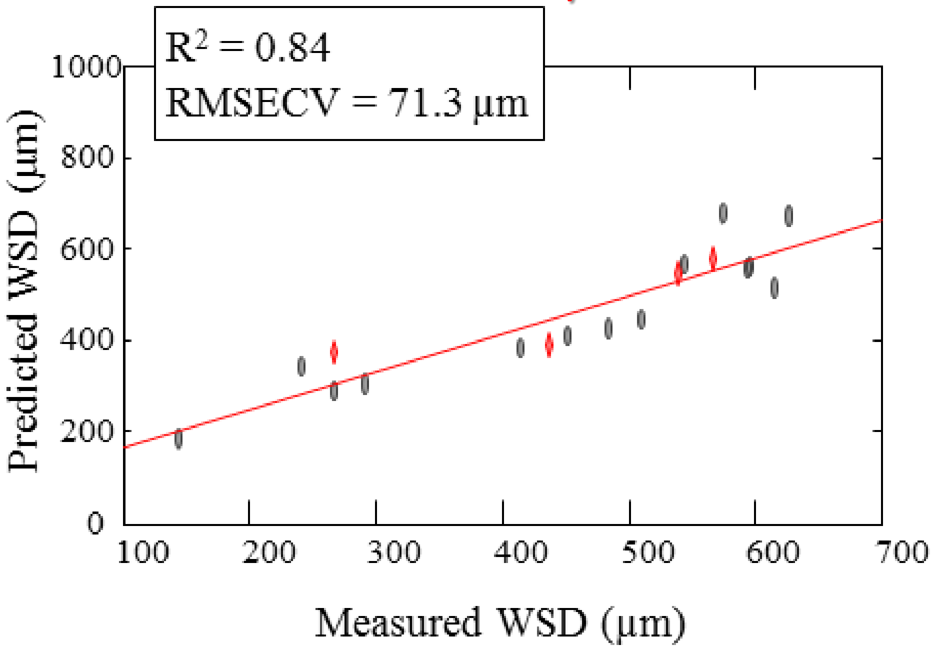
- Lubricity predictions using NMR and GC-FIMS data
- Partial least squares (PLS) regression model
- Describes correlations to sub-structure, i.e.:
  - Positive – methylene > 4 carbons from a terminal methyl or branch point
  - Negative – hydroaromatics like tetralins and naphthenes
- Approach is amenable to other fuel performance properties
- Future comparisons will leverage PNNL investments in signature discovery to make correlations

ASTM D6079 HFRR Lubricity Measurements



WSD is Wear Scar Diameter
Gray ovals are training set; Red diamonds are cross-validation data.

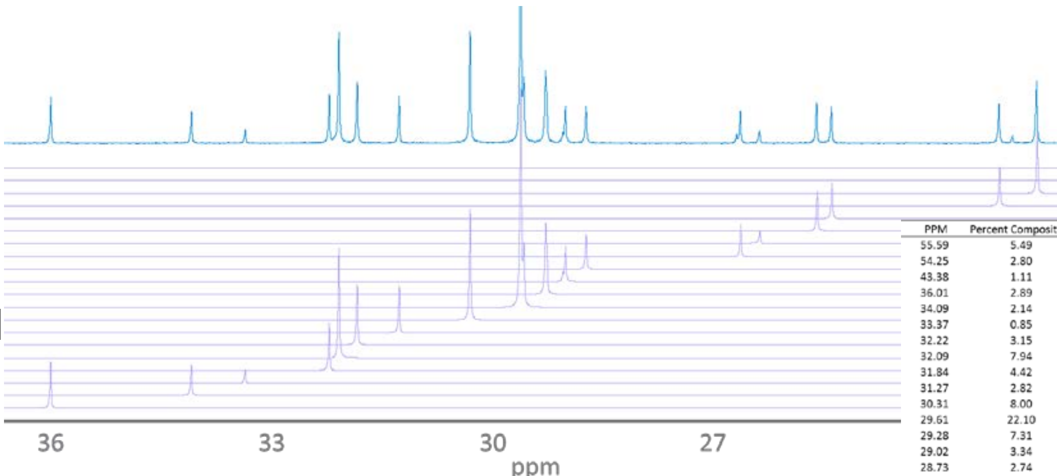
Conclusion: *PLS correlation of NMR and GC data can provide a methodology that can predict fuel property effects and long-term impacts on engine fuel systems.*

Diesel sample set obtained and analyzed in collaboration with CanmetENERGY.
GC-FIMS data provided by CanmetENERGY..

Technical Accomplishments
-- Signal Processing

- Complete Reduction to Amplitude-Frequency Table (CRAFT)
  - Application of CRAFT processing to NMR spectra of fuels
  - Leverage signal processing techniques developed for metabolomics research
- Utilizes time and frequency domain data to deconvolve complex NMR spectra
- Quantitative chemical, or sub-structural compositions
- Spectral modeling allows accurate reconstruction of key spectral regions
- Rapid signal processing holds promise for application to process measurements

CRAFT Analysis of a $^{13}C\{^1H\}$ NMR Spectrum Showing Models Extracted from an 8-Component, Diesel Fuel Surrogate



PPM	Percent Composition
55.59	5.49
54.25	2.80
43.38	1.11
36.01	2.89
34.09	2.14
33.37	0.85
32.22	3.15
32.09	7.94
31.84	4.42
31.27	2.82
30.31	8.00
29.61	22.10
29.28	7.31
29.02	3.34
28.73	2.74
26.63	2.09
26.36	1.00
25.59	2.93
25.39	2.66
23.11	3.02
22.60	4.53
19.26	1.40
19.10	0.73
14.03	4.56

Conclusion: *Advanced data processing algorithm allows extraction of quantitative spectral data, which can be readily utilized by predictive tools developed for structure-property correlation.*

Surrogate diesel sample and pure components obtained and analyzed as part of the CRC Improved Diesel Surrogate Fuels for Engine Testing and Kinetic Modeling Project

Responses to Previous Year Reviewers' Comments

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- This project was not reviewed last year.

Collaboration and Coordination

- **Coordinating Research Council (CRC)**
  - Contributor
    - Fuels for Advanced Combustion Engines (FACE) Working Group
    - Improved Diesel Surrogate Fuels for Engine Testing and Kinetic Modeling (AVFL-18/18a)
    - Characterization of Alternative and Renewable Fuels (AVFL-19/19a)
  - Participant
    - FACE Diesel Fuels Data Mining (AVFL-23)
    - Measuring Fuel Heat of Vaporization (AVFL-27)

- **CanmetENERGY**
  - Fuels separations work (i.e., GC x GC, GC-FIMS, etc.)
  - Fuel property modeling

AVFL refers to the Advanced Vehicle/Fuels/Lubricants Committee of the CRC, www.crcao.com. The associated number refers to specific projects sponsored by AVFL.

Remaining Challenges and Barriers

- **Fuel structure-property correlations have previously been undertaken. Weaknesses for these correlations which remain include:**
  - Extending correlations beyond the fuel set being studied.
  - Developing correlations that can be interpreted and acted upon.

- **Obtaining relevant fuel sets that are sufficiently representative to provide meaningful conclusions, such as:**
  - Fuels must be un-additized when analyses are made. Depends upon additive concentration and analysis method.
  - Fuel sets should not be esoteric, unless the purpose is to show relationships to other fuel sets.

Proposed Future Work

- **Continue to develop signal processing and correlation approaches to relate fuel properties and chemical structures.**
  - Evaluate whether CRAFT signal processing results can be extended beyond surrogate fuel sets.
  - Integrate CRAFT results into structure-property correlation approaches.
  - Refine correlation approaches to extend structure-property correlations beyond lubricity, maximizing the use of available fuel sets.
- **Introduce additional fuels sets when available through our collaborations.**
- **Lubricity Correlations --** Complete publication using PLS regression to correlate fuel sub-structures to lubricity. Include challenge data from as many fuel sets as possible to validate the predictive tool.
- **Shale Oil Data Set --** Complete publication highlighting structure/sub-structure changes during upgrading.

Summary

- **The goal of this research is to identify chemical substructures in fuels using analytical tools and relate them to performance properties using correlation techniques. We have focused on:**
  - Applying advanced analytical techniques to identifying important chemical sub-structures in fuel.
  - Applying processing and correlation methodologies to fuels research.

- **We have made significant technical progress by**
  - Correlating lubricity to specific fuel substructures.
  - Identifying and quantifying tertiary carbon contributions to fuels, specifically with respect to gum and peroxide formation, both deleterious to engine operation.
  - Working with collaborators to quantify carbon types most relevant to surrogate diesel fuels.
  - Obtaining sub-structure data sets for several alternative and renewable fuels in preparation for further analysis.

Backup Slides

Expanded 2D NMR Spectrum
– Aliphatic Region D7814, GTL Diesel Fuel

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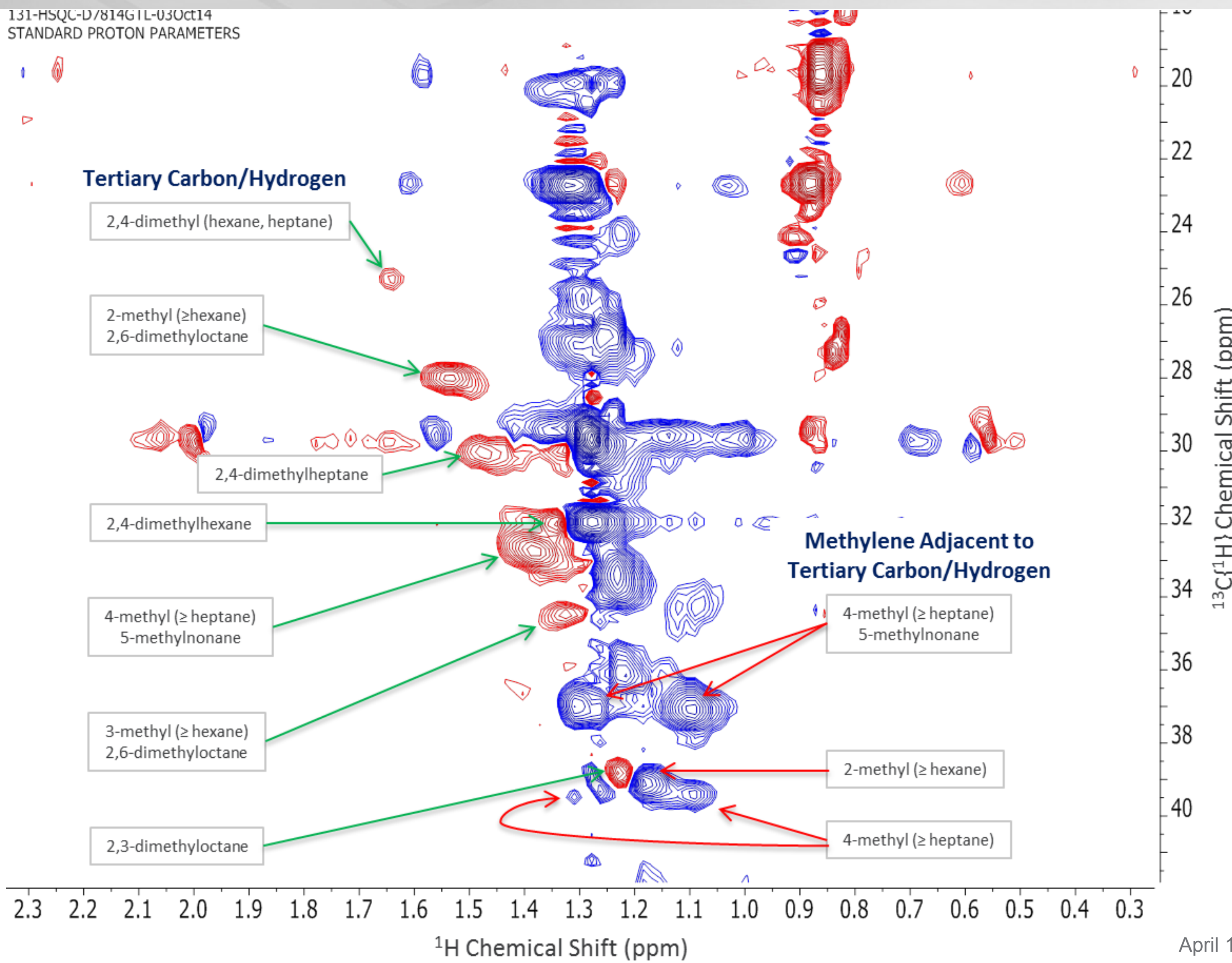

ULSD sample obtained and analyzed as part of the CRC Advanced Alternative Renewable Fuels and the Surrogate Diesel Fuels Projects

2D-NMR Spectrum
– Aromatic Region of EcoShale™

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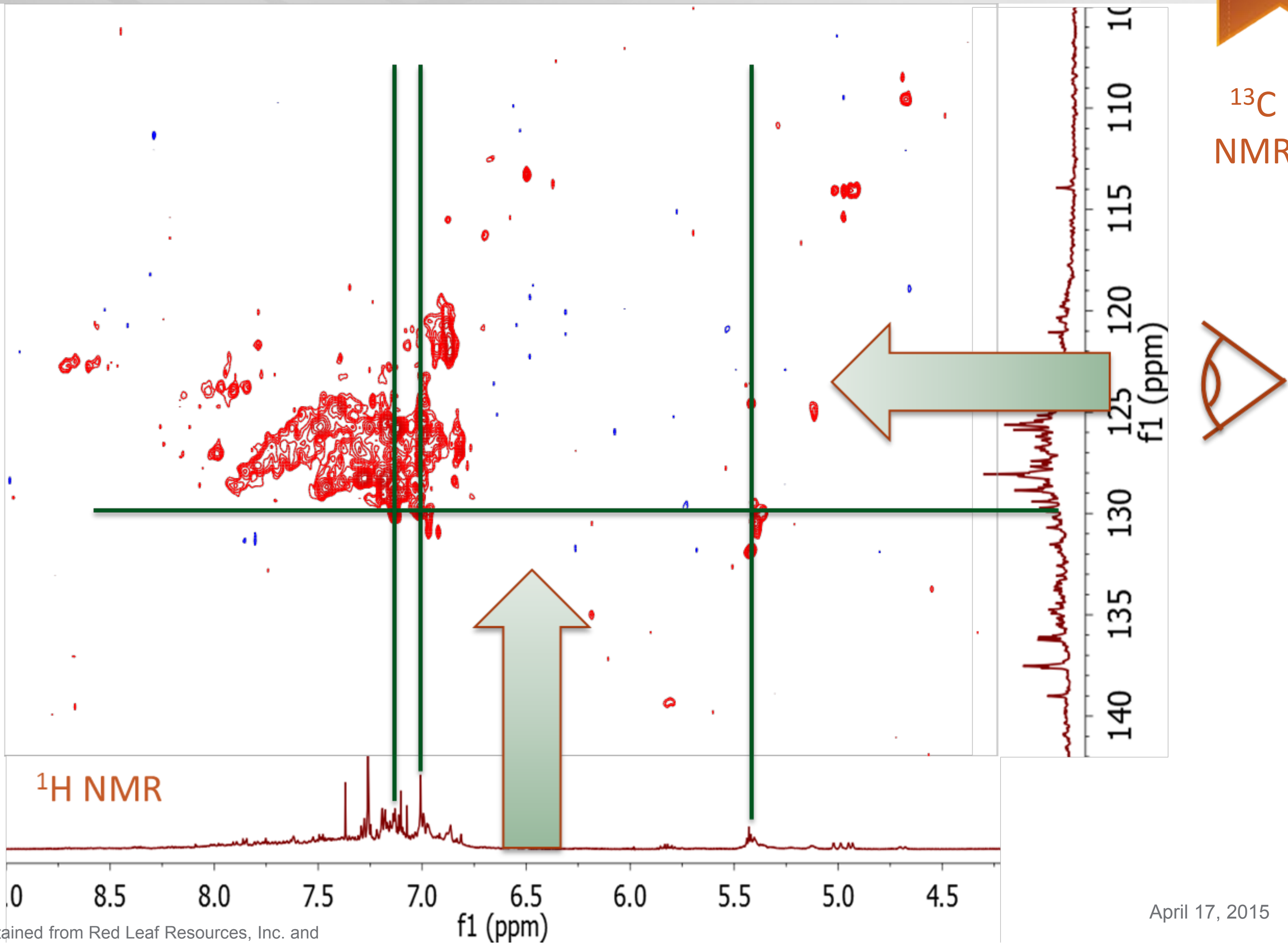
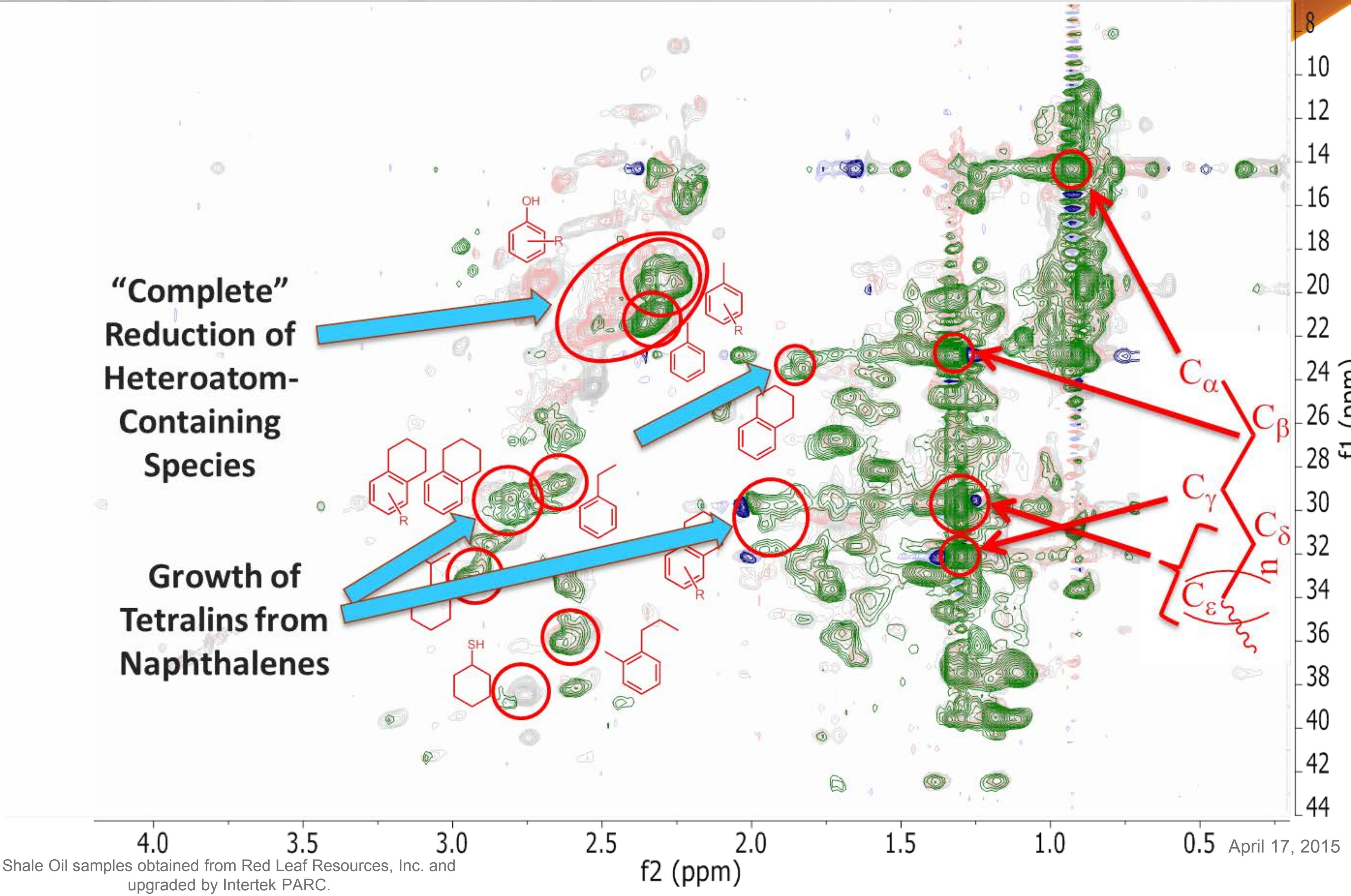


Shale Oil samples obtained from Red Leaf Resources, Inc. and upgraded by Intertek PARC.

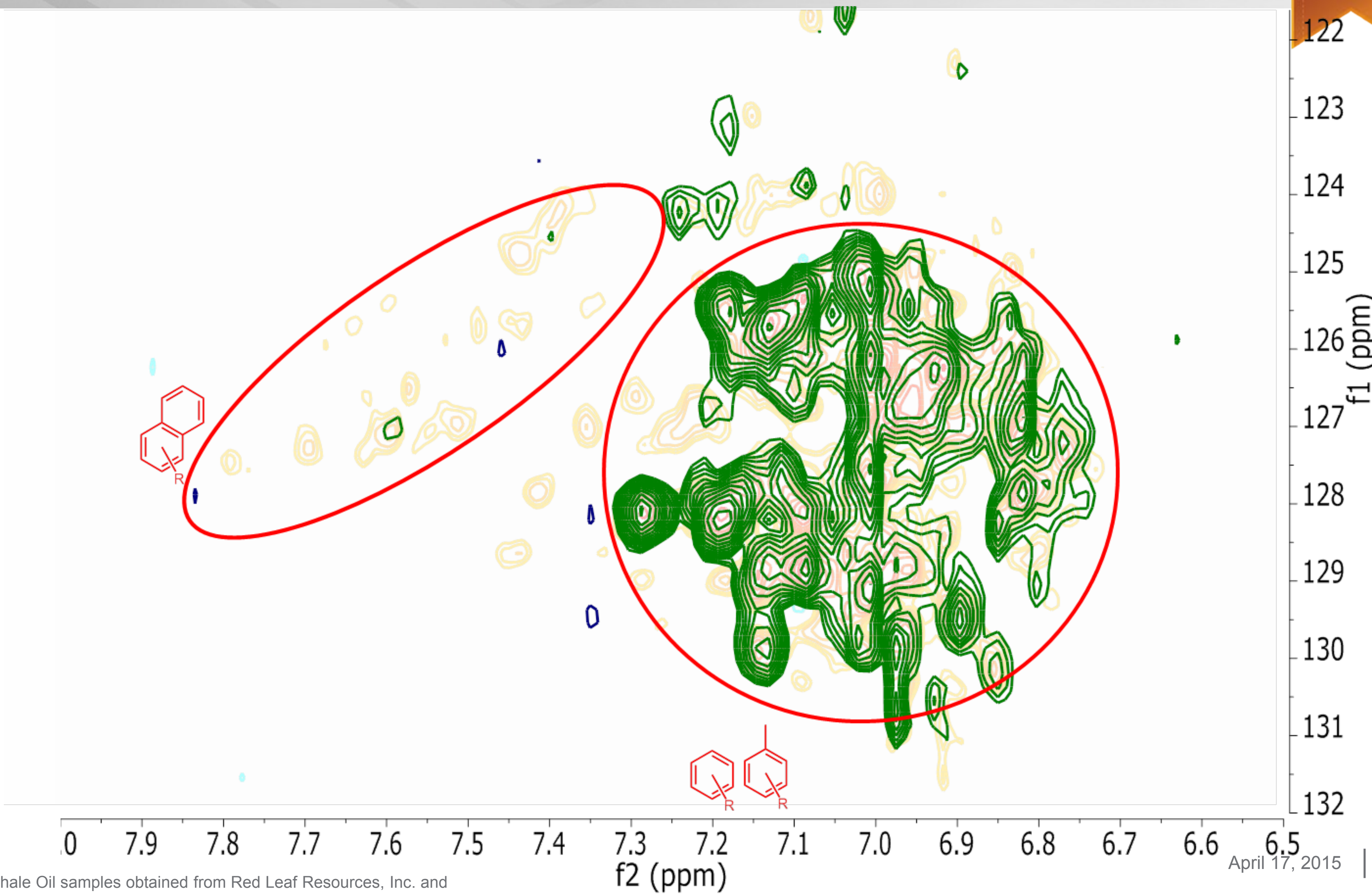
HSQC NMR Spectrum

– Aliphatic Region of Fully Hydrotreated Shale Oil Diesel #2



Shale Oil samples obtained from Red Leaf Resources, Inc. and upgraded by Intertek PARC.

HSQC NMR Spectrum, Aromatic Region – Overlay of Shale Oil Diesel #2 with Commercial Diesel



Shale Oil samples obtained from Red Leaf Resources, Inc. and upgraded by Intertek PARC.

Fuel Sample Sets Obtained Through Our Collaborations

		# of		Data Collection					Paper			Report			
				NMR			GC*								
	Fuel Set	Samples	Source	^{1}H	^{13}C	HSQC	GC FIMS	GC x GC	Review	Draft	Final	Review	Draft	Final	Comments
1	F6	4 (28)	Canmet-ENERGY	X	X		X			X					4 unique fuels each fractionated by boiling point range to match viscosities. Being used for lubricity modeling. Regression modeling is complete. Paper ETA = FY15
2	FACE Gasoline	10	CRC	X	X				X			X			Gasoline fuels blended to meet targeted properties. Will be used for structure-property correlation, using property testing conducted by other FACE Working Group members. Paper or report under review. Data may fold into other documents rather than stand alone
3	FACE Diesel	12	CRC	X	X	IP	X	X	X					X	Diesel fuels blended to meet targeted properties. Will be used for structure-property correlation, using property testing conducted by other FACE Working Group members.
4	Advanced and Renewable	12	CRC	X	X	IP	X	X	X					X	Diesel fuels representing renewable or unconventional fuel sources. Will be used for structure-property correlation, using property testing conducted by other FACE Working Group members. Through an internal PNNL investment, we are applying non-traditional mathematical correlation approaches to seek relationships between structure and properties not apparent using mainstream regression modeling.
5	Shale Oil	10	Red Leaf Resources	X	X	IP	IP	IP		X					Shale oil-derived samples. Samples include two diesel fuels, 1-shale oil sample, 1-stabilized and 2-mildly hydrotreated shale oil samples, and 4-distillate cuts derived from shale oil. Oral presentation and proceedings paper presented at the August 2014 American Chemical Society Fuels Division. Working towards a fuel characterization publication. Paper ETA = FY15
6	Renewable Naphtha and Gasoline Samples	5	CRC	X	X	IP	X	X					X		Draft report underway.
7	EPA Gasoline Samples	6	EPA	X	X	IP		X					X		Draft report underway.
8	AVFL-18a Surrogate Diesels	5	CRC	IP	IP	IP		X	X			X			Data is being taken now. We are examining other fuel groups to assist with validating our selections of surrogate fuel components. In addition to carbon-type analysis, we expect to provide information on the quantities of 2-methyl alkane components in diesel fuels. Both sets of data will be presented, probably as a report, but certainly included in our surrogate fuels publication(s).

*GC x GC and GC FIMS are being run by CanmetENERGY. We are collaboratively using their data. Additionally, we are working with CanmetENERGY to better utilize PNNL's GC x GC capability.
X = complete.
IP = in progress.